02078 US
non-provisional

Description

GAS GENERATING COMPOSITION FOR INFLATOR CONTAINING MELAMINE CYANURATE

Technical Field to Which The Invention Belongs

The present invention relates to a gas generating composition which is suitable for air bag restraining system in automobiles and the like, its molded article and an air bag inflator using the same.

Prior Art

Conventionally, compositions using sodium azide have been often used as a gas generating agent for an air bag which serves as an occupant protecting apparatus in an automobile. However, as the toxicity to human body [LD50(oral-tat) = 27mg/kg] and danger in handling of sodium azide is becoming problems, gas generating compositions containing various kinds of nitrogen-containing organic compounds have been developed as so-called non-azide based gas generating compositions which are safer alternatives.

US-B No.4,909,549 discloses a composition comprising a hydrogen-containing tetrazole, a triazole compound and an oxygen-containing oxidant. US-B No.4,370,181 discloses a gas generating composition comprising a metal salt of bitetrazole not containing hydrogen and an oxidant not containing oxygen. US-B No.4,369,079 discloses a gas generating composition comprising a metal salt of bitetrazole not containing hydrogen,

alkaline metal nitrate, alkaline metal nitrite, alkaline earth metal nitrate, alkaline earth metal nitrite and a mixture thereof. US-B No.5,542,999 discloses a gas generating agent comprising a fuel such as GZT, TAGN (triaminonitroguanidine), NG (nitroguanidine), NTO and the like, basic copper nitrate, a catalyst which reduces toxic gas and a coolant agent. JP-A No. 10-72273 discloses a gas generating agent comprising a bitetrazole metal salt, a bitetrazole ammonium salt, aminotetrazole and ammonium nitrate. JP-A No. 2001-220282 discloses a gas generating agent comprising a triazine derivative and a basic metal nitrate.

The above non-azide based gas generating compositions, however, have problems in respect of combustion temperature, burning rate, phase transition, amounts of generated carbon monoxide and nitrogen oxide, gas output, safety in handling and the like.

The gas generating composition disclosed in US-B No.4,369,079 has a high combustion temperature, and hence require a large amount of coolant in practical use. The composition of US-B No.5,542,999 has a small burning rate, and therefore, there is a possibility such that it is not burnt completely in a short period of time. As to the gas generating agent in JP-A No. 10-72273, a molded article of a gas generating composition is broken due to a form change caused by phase transition of ammonium nitrate in the use temperature range, so that stable combustion cannot be obtained. In the patents of non-azide based gas generating agents other than JP-A No.

2001-220282, tetrazoles, nitroguanidine, TAGN and the like are used as a fuel for gas generating agent, but they are dangerous substances and has to be handled with special attention.

In addition, there is no prior art, including the invention disclosed in JP-A No. 2001-220282, that uses melamine cyanurate as a fuel of a gas generating agent.

Disclosure of the Invention

Accordingly, an object of the present invention is to provide a gas generating composition having a low combustion temperature, generating only small amounts of carbon monoxide and nitrogen oxide and being safe in handling, and a molded article thereof, as well as an inflator for air bag using the same.

The present invention provides a gas generating composition comprising Component (a) as described below, and Component (b) if required:

(a) melamine cyanurate or a mixture of melamine cyanurate and nitrogen-containing organic compound serving as a fuel.

(b) oxygen-containing oxidant.

In the above aspect of the invention, although the gas generating composition may comprise Component (a) but not Component (b), the gas generating composition preferably comprises both Component (a) and Component (b).

Furthermore, the present invention provides a molded article in a shape of a single-perforated cylinder, a perforated (porous) cylinder or a pellet obtained from the above gas generating composition. The single pore or multi pores may be

a through hole or a non-through hole.

Furthermore, the present invention provides an inflator for air bag using the above gas generating composition and the molded article.

Since the gas generating composition and its molded article according to the present invention are low in toxicity and less dangerous, so that they are safe in handling, and have a large burning rate, a low combustion temperature and small amounts of generated carbon monoxide and nitrogen oxide at the time of combustion.

Preferred Embodiment of The Invention

Melamine cyanurate or a mixture of melamine cyanurate and nitrogen-containing organic compound of Component (a) used in the present invention is low in toxicity, and is preferably combined with Component (b) because low combustion temperature and large burning rate can be obtained.

Melamine cyanurate is desirable because it has such low toxicity of LD50 (oral-rat)=2020 mg/kg and excellent thermal stability, and is safe in handling and inexpensive.

An example of the nitrogen-containing organic compound can be one or at least two selected from the group consisting of tetrazole compounds including 5-aminotetrazole and bitetrazole ammonium salt; guanidine compounds including nitroguanidine, guanidine nitrate and dicyanediamide; and triazine compounds including melamine, trimethylol melamine, alkylated methylol melamine, ammeline, ammelande, nitrate salt of melamine, perchlorate salt of melamine, trihydrazino

triazine and nitrated compound of melamine.

In view of solving the problem of the invention, the blending ratio (mass ratio) of nitrogen-containing organic compound/melamine cyanurate in preparing a mixture of melamine cyanurate and a nitrogen-containing organic compound is preferably 0.05 to 8, more preferably 0.1 to 6, and still more preferably 0.2 to 2.

An example of the oxygen-containing oxidant of Component (b) used in the present invention can be one or at least two selected from the group consisting of metal nitrates, ammonium nitrate, metal perchlorates, ammonium perchlorate, metal nitrites, metal chlorates, basic copper nitrate, basic cobalt nitrate, basic zinc nitrate and basic manganese nitrate, and among these, basic copper nitrate is preferable.

The basic copper nitrate has excellent thermal stability because phase transition does not occur in the use temperature range and it has a high melting point. In addition, since it acts to lower the combustion temperature of gas generating agent, an amount of generated nitrogen oxide can also be reduced.

In case of making the gas generating composition of the present invention two-component system consisting of Component (a) and Component (b), the content of Component (a) is preferably 10 to 60% by mass, and more preferably 15 to 50% by mass. The content of Component (b) is preferably 40 to 90% by mass, and more preferably from 50 to 85% by mass.

One preferred embodiment of the gas generating composition of two-component system comprises (a) melamine cyanurate and

(b) basic copper nitrate. In this case, the content of (a) melamine cyanurate is preferably 15 to 40% by mass and the content of (b) basic copper nitrate is preferably 60 to 85% by mass.

Another preferred embodiment of the gas generating composition of two-component system comprises (a) a mixture of melamine cyanurate and guanidine nitrate and (b) basic copper nitrate. In this case, the content of (a) a mixture of melamine cyanurate and guanidine nitrate is preferably 15 to 60% by mass and the content of (b) basic copper nitrate preferably is 40 to 85% by mass.

Another preferred embodiment of the gas generating composition of two-component system comprises (a) a mixture of melamine cyanurate and melamine and (b) basic copper nitrate. In this case, the content of (a) a mixture of melamine cyanurate and melamine is preferably 15 to 50% by mass and the content of (b) basic copper nitrate is preferably from 50 to 85% by mass.

Another preferred embodiment of the gas generating composition of two-component system comprises (a) a mixture of melamine cyanurate and bitetrazole ammonium salt and (b) basic copper nitrate. In this case, the content of (a) a mixture of melamine cyanurate and bitetrazole ammonium salt is preferably 15 to 50% by mass and the content of (b) basic copper nitrate is preferably 50 to 85% by mass.

When the gas generating composition of the present invention is prepared by one-component system of Component (a), two-component system of Components (a) and (b), or three-component system of Components (a), (b) and (d), if the molding

strength of the molded article is not sufficient, there may be a possibility such that the molded article collapses and burns too violently to control the combustion in actual combustion. For this reason, a binder of Component (c) is preferably added.

The binder of Component (c) can be one or at least two selected from the group consisting of carboxymethyl cellulose (CMC), sodium carboxymethyl cellulose (CMCNa), potassium carboxymethyl cellulose, ammonium carboxymethyl cellulose, cellulose acetate, cellulose acetate butylate (CAB), methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), ethylhydroxyethyl cellulose (EHEC), hydroxypropyl cellulose (HPC), carboxymethylethyl cellulose (CMEC), microcrystal cellulose, polyacrylamide, amino compound of polyacrylamide, polyacrylhydrazide, acrylamide/acrylic acid metal salt copolymer, polyacrylamide/polyacrylic acid ester compound copolymer, polyvinyl alcohol, acrylic rubber, guar gum, starch and silicone. Among these, sodium carboxymethyl cellulose (CMCNa) and guar gum are preferable in view of the adherence of the binder, cost, ignitionability and the like.

When the gas generating composition of the present invention is prepared by a one-component system of Component (a), two-component system of Components (a) and (b), or three-component system of Components (a), (b) and (c), it is preferable to further add an additive of Component (d) in order to adjust the burning rate of gas generating agent and clean the combustion gas.

The additive of Component (d) can be at least one selected

from the group consisting of metal oxides such as copper (II) oxide, iron oxide, zinc oxide, cobalt oxide, manganese oxide, molybdenum oxide, nickel oxide, bismuth oxide, silica, alumina; metal hydroxides such as aluminum hydroxide, magnesium hydroxide, cobalt hydroxide, iron hydroxide; metal carbonates or basic metal carbonates such as cobalt carbonate, calcium carbonate, basic zinc carbonate, basic copper carbonate; complex compounds of metal oxides or hydroxides such as Japanese acid clay, kaolin, talc, bentonite, diatomaceous earth, hydrotalcite; metal acid salts such as sodium silicate, mica molybdate, cobalt molybdate, ammonium molybdate; silicone, molybdenum disulfide, calcium stearate, silicon nitride, silicon carbide, metaboric acid, boric acid and boric anhydride.

For reducing an amount of generated carbon monoxide after combustion of the gas generating composition, it is preferred to add aluminum hydroxide or cobalt oxide as Component (d).

When the gas generating composition of the present invention is prepared by three-component system or four-component system of Components (a) to (d), the contents of the respective components are as follows: the content of Component (a) is preferably 10 to 60% by mass and more preferably 10 to 50% by mass; the content of Component (b) is preferably 40 to 90% by mass, and more preferably 50 to 80% by mass; the content of Component (c) is preferably 0 to 15% by mass, and more preferably 1 to 10% by mass; and the content of Component (d) is preferably not more than 20% by mass, and more preferably 0.5 to 15% by mass.

One preferred embodiment of the gas generating composition of three-component system comprises melamine cyanurate of Component (a) and basic copper nitrate of Component (b) and sodium carboxymethyl cellulose or guar gum of Component (c). In this case, the content of melamine cyanurate of Component (a) is preferably 15 to 30% by mass, basic copper nitrate of Component (b) is preferably 40 to 90% by mass and sodium carboxymethyl cellulose or guar gum of Component (c) is preferably 0.1 to 10% by mass.

Another preferred embodiment of the gas generating composition of three-component system comprises a mixture of melamine cyanurate and guanidine nitrate of Component (a) and basic copper nitrate of Component (b) and sodium carboxymethyl cellulose or guar gum of Component (c). In this case, the content of a mixture of melamine cyanurate and guanidine nitrate of Component (a) is preferably 15 to 50% by mass, basic copper nitrate of Component (b) is preferably 50 to 80% by mass and sodium carboxymethyl cellulose or guar gum of Component (c) is preferably 0.1 to 10% by mass.

Another preferred embodiment for the gas generating composition of three-component system comprises a mixture of melamine cyanurate and melamine of Component (a) and basic copper nitrate of Component (b) and sodium carboxymethyl cellulose or guar gum of Component (c). In this case, the content of a mixture of melamine cyanurate and melamine of Component (a) is preferably 15 to 30% by mass, basic copper nitrate of Component (b) is preferably 60 to 80% by mass and sodium carboxymethyl cellulose

or guar gum of Component (c) is preferably 0.1 to 10% by mass.

One preferred embodiment of the gas generating composition of four-component system comprises melamine cyanurate of Component (a), basic copper nitrate of Component (b), sodium carboxymethyl cellulose of Component (c) and aluminum hydroxide of Component (d). In this case, the content of melamine of Component (a) is preferably 10 to 30% by mass, basic copper nitrate of Component (b) is preferably 40 to 90% by mass, sodium carboxymethyl cellulose of Component (c) is preferably 0.1 to 10% by mass, and aluminum hydroxide of Component (d) is preferably 0.5 to 15% by mass.

Another preferred embodiment for the gas generating composition of four-component system comprises a mixture of melamine cyanurate and guanidine nitrate of Component (a), basic copper nitrate of Component (b), sodium carboxymethyl cellulose of Component (c) and aluminum hydroxide of Component (d). In this case, the content of a mixture of melamine cyanurate and guanidine nitrate of Component (a) is preferably 10 to 50% by mass, basic copper nitrate of Component (b) is preferably 40 to 90% by mass, sodium carboxymethyl cellulose of Component (c) is preferably 0.1 to 10% by mass, and aluminum hydroxide of Component (d) is preferably 1 to 10% by mass.

Another preferred embodiment for the gas generating composition of four-component system comprises a mixture of melamine cyanurate and melamine of Component (a), basic copper nitrate of Component (b), sodium carboxymethyl cellulose of Component (c) and aluminum hydroxide of Component (d). In this

case, the content of a mixture of melamine cyanurate and melamine of Component (a) is preferably 10 to 30% by mass, basic copper nitrate of Component (b) is preferably 40 to 90% by mass, sodium carboxymethyl cellulose of Component (c) is preferably 0.1 to 10% by mass, and aluminum hydroxide of Component (d) is preferably 0.1 to 15% by mass.

Another preferred embodiment for the gas generating composition of four-component system comprises melamine cyanurate of Component (a), basic copper nitrate of Component (b), sodium carboxymethyl cellulose of Component (c) and magnesium hydroxide or metaboric acid of Component (d). In this case, the content of melamine cyanurate of Component (a) is preferably 10 to 30% by mass, basic copper nitrate of Component (b) is preferably 40 to 90% by mass, sodium carboxymethyl cellulose of Component (c) is preferably 0.1 to 10% by mass, and magnesium hydroxide or metaboric acid of Component (d) is preferably 1 to 10% by mass.

Another preferred embodiment for the gas generating composition of four-component system comprises melamine cyanurate of Component (a), basic copper nitrate of Component (b), sodium carboxymethyl cellulose of Component (c) and one or at least two additives selected from the group consisting of aluminum oxide, silica, Japanese acid clay and diatomaceous earth of Component (d). In this case, the content of melamine cyanurate of Component (a) is preferably 10 to 30% by mass, basic copper nitrate of Component (b) is preferably 50 to 80% by mass, sodium carboxymethyl cellulose of Component (c) is preferably

0.1 to 10% by mass, and the additive of Component (d) is preferably 0.1 to 10% by mass.

The gas generating composition of the present invention can be molded into a desired shape such as a single-perforated cylinder, a perforated (porous) cylinder or a pellet. These molded articles can be produced by adding and mixing water or an organic solvent into the gas generating composition, and then extrusion-molding this (in case of a single-perforated cylinder or a perforated (porous) cylinder) or compression-molding this with pelletizer (in case of a pellet).

The gas generating composition according to the present invention or the molded article obtained therefrom can be applied in various kinds of vehicles to an inflator for an air bag for a driver side, inflator for an air bag for passenger side, inflator for an air bag for side collision, inflator for a inflatable curtain, inflator for a knee bolster, inflator for inflatable a seat belt, inflator for a tubular system and a gas generator for a pretensioner.

Furthermore, inflators using the gas generating composition of the present invention or the molded article obtained therefrom may be either pyrotechnic type in which gas is supplied only from a gas generating agent or hybrid type in which gas is supplied from both compressed gas such as argon and gas generating agent.

Furthermore, the gas generating composition of the present invention or the molded article obtained therefrom can also be used as an igniting agent called as an enhancer agent (or booster)

for transmitting energy of a detonator or squib to a gas generating agent.

Examples

In the followings, the present invention will be described in detail by way of Examples, however, the present invention is not limited to these Examples.

Examples 1 to 18, Comparative examples 1 and 2

Gas generating compositions having compositions shown in Table 1 were produced. Combustion temperature, gas output (the unit mol/100 g represents the number of moles of generated gas per 100 g of composition), and amounts of generated CO and NO of these compositions determined by theoretical calculation are shown in Table 1.

Table 1

	Composition (composition ratio: % by mass)	Combustion temperature (k)	Gas output (mol/100g)	Generated amount of CO (mol/100g)	Generated amount of NO (mol/100g)
Example 1	MC/BCN (26.16/73.84)	1348	2.15	1.31×10^{-4}	0
Example 2	MC/BCN/CMCNa (23.09/73.91/3)	1358	2.14	1.4×10^{-2}	0
Example 3	MC/BCN/CMCNa/$Al(OH)_3$ (22.31/71.69/3/3)	1294	2.14	1.3×10^{-2}	0
Example 4	MC/BCN/CMCNa/$Al(OH)_3$ (21.79/70.21/3/5)	1251	2.13	1.2×10^{-2}	0
Example 5	MC/BCN/CMCNa/$Al(OH)_3$ (17.24/70.76/7/5)	1298	2.09	1.3×10^{-2}	0
Exampl 6	MC/GN/BCN (21.29/10/68.71)	1390	2.32	1.3×10^{-3}	0
Example 7	MC/GN/BCN (16.39/20/63.61)	1493	2.48	1.32×10^{-3}	0
Example 8	MC/GN/BCN (6.59/40/53.41)	1674	2.80	1.50×10^{-2}	2.76×10^{-5}
Example 9	MC/Melamine/BCN (24.93/1/74.07)	1357	2.15	1.05×10^{-3}	0
Example 10	MC/GN/BCN/CMCNa (18.37/5/71.63/5)	1379	2.20	1.4×10^{-2}	0
Example 11	MC/GN/BCN/CMCNa (15.92/10/69.08/5)	1432	2.28	1.4×10^{-2}	0
Example 12	MC/GN/BCN/CMCNa (11.02/20/63.98/5)	1532	2.44	1.4×10^{-2}	0
Example 13	MC/Melamine/BCN/CMCNa (17.05/3/74.95/5)	1358	2.11	1.4×10^{-2}	0
Example 14	MC/GN/BCN/CMCNa/$Al(OH)_3$ (14.61/10/65.39/5/5)	1358	2.27	1.3×10^{-2}	0
Example 15	MC/GN/BCN/CMCNa/$Al(OH)_3$ (9.71/20/60.29/5/5)	1429	2.43	1.3×10^{-2}	
Example 16	MC/Melamine/BCN/CMCNa/$Al(OH)_3$ (15.74/3/71.26/5/5)	1307	2.11	1.3×10^{-2}	
Example 17	MC/GN/BCN/$Al(OH)_3$ (20.3/10/64.7/5)	1325	2.32	1.2×10^{-2}	
Example 18	MC/GN/BCN/$Al(OH)_3$ (15.4/20/59.6/5)	1376	2.48	1.2×10^{-2}	
Comparative example 1	BHTK/KNO_3 (51.44/48.56)	2393	1.26	5.1×10^{-4}	4.1×10^{-3}
Comparative example 2	NaN_3/CuO (61/39)	1421	1.41	0	1.3×10^{-6}

In Table 1, "MC" denotes melamine cyanurate, "GN" guanidine nitrate, "BCN" basic copper nitrate, "CMCNa" sodium carboxymethyl cellulose and "BHTK" potassium bitetrazole. The same denotations are used in other tables.

Combustion temperatures of Examples 1 to 18 were lower than that of Comparative example 1 of non-azide based gas generating agent. As to Examples 1 to 14, a theoretical amount of generated NO was zero, showing that they were more effective in reducing an amount of generated NO than Comparative Examples 1 and 2. In Examples 1 to 18, gas output is improved by 40% or more compared with Comparative Example 2 of azide based gas generating agent.

Examples 19 to 24

Gas generating compositions having compositions shown in Table 2 were produced. Friction sensitivity and drop hammer sensitivity of these compositions were tested according to the explosives performance test method of JIS K4810-1979. The results are shown in Table 2.

Table 2

	Composition (composition ratio: % by mass)	Friction sensitivity (N)	Drop hummer sensitivity (cm)
Examples 19	MC/BCN/(26.16/73.84)	>353	>100
Examples 20	MC/BCN/CMCNa (23.09/73.91/3)	>353	>100
Examples 21	MC/BCN/CMCNa/$Al(OH)_3$ (22.31/71.69/3/3)	>353	>100
Examples 22	MC/GN/BCN/$Al(OH)_3$ (20.3/10/64.7/5)	>353	60-70
Examples 23	MC/GN/BCN/CMCNa/$Al(OH)_3$ (9.71/20/60.29/5/5)	>353	60-70
Examples 24	MC/Melamine/BCN/CMCNa (17.05/3/74.95/5)	>353	>100

In Examples 19 to 24, friction sensitivities exceeded 353 N and drop hammer sensitivities are more than 60 cm, suggesting that friction and drop hammer sensitivities are insensitive, and hence safety in handling is high.

Examples 25 to 27

Gas generating compositions having compositions shown in Table 3 were produced. For these gas compositions, melting temperature, exothermic decomposition starting temperature and TG weight reduction starting temperature were measured using a TAS-type differential thermal analyzer (produced by Rigaku Corporation). The temperature raising speed during measurement was 20°C/min, the measurement atmosphere was nitrogen gas, and the sample amount in measurement was 1 to 2 mg. The results are shown in Table 3.

Table 3

	Composition (Composition ratio: % by mass)	Melting temperature (°C)	Exothermic decomposition starting temperature (°C)	Weight reduction starting temperature (°C)
Example 25	MC (100)	280	-	284
Example 26	MC/BCN (26.16/73.84)	220	250	226
Example 27	MC/BCN/CMCNa (23.09/73.91/3)	210	239	212

In Examples 25 to 27, melting temperature, exothermic decomposition starting temperature and weight reduction starting temperature were 200°C or more, suggesting excellent thermal stability.

Examples 28 to 29

Gas generating compositions having formulations shown in Table 4 were produced. These compositions were molded into a strand, and a burning rate was measured under nitrogen atmosphere at pressures of 4900, 6860, 8820 kPa. The burning rate at 6860 kPa, and pressure index between 4900 and 8820 kPa are shown in Table 4. Pressure index was determined from the following formula: rb= αP^n (wherein, rb: burning rate, α: coefficient, P: pressure and n: pressure index).

Table 4

	Composition (composition ratio: % by mass)	Burning rate (mm/sec)	Pressure index
Example 28	MC/BCN/CMCNa (23.09/73.91/3)	9. 95	0.23
Example 29	MC/BCN/CMCNa/$Al(OH)_3$ (22.31/71.69/3/3)	8.68	0.31

As is apparent from the above, each numerical value shown in Examples 28 to 29 shows that practical requirement required for a gas generating composition for inflator gas is satisfied.